(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 1 104 799 A1

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
06.06.2001 Bulletin 2001/23

(51) Int Cl.[7]: **C09K 11/79**

(21) Application number: **99123747.0**

(22) Date of filing: **30.11.1999**

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE
Designated Extension States:
AL LT LV MK RO SI

(71) Applicant: **Patent-Treuhand-Gesellschaft für elektrische Glühlampen mbH**
81543 München (DE)

(72) Inventors:
- **Hintzen,H.T.,**
Lab.of Solid State & Materials Chem.
5600 MB Eindhoven (NL)
- **van Krevel,J.W.H.,**
Lab.Solid State&Materials Chem.
5600 MB Eindhoven (NL)
- **Botty, G.,Ir. Oce Technologies B.V.**
5900 MA Venlo (NL)

(54) **Red emitting luminescent material**

(57) Red emitting luminescent material with a host lattice of the nitridosilicate type $M_xSi_yN_z$:Eu, wherein M is at least one of an alkaline earth metal chosen from the group Ca, Sr, Ba and wherein z = 2/3x + 4/3y.

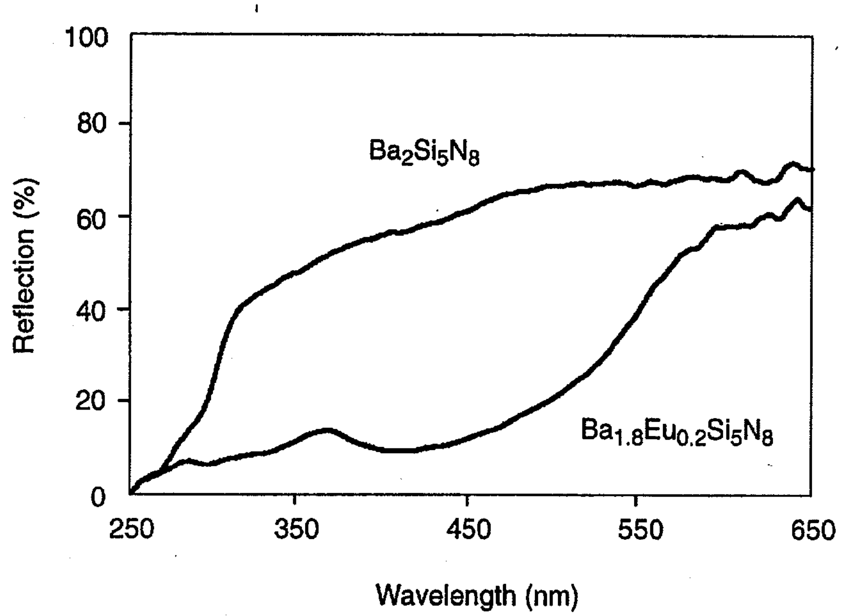

FIG. 1

EP 1 104 799 A1

Description

Technical Field

[0001] This invention relates to a Red Emitting Luminescent Material and more particularly, but not exclusively to a phosphor for light sources, especially for Light Emitting Devices (LED). The phosphor belongs to the class of rare-earth activated silicon oxynitrides.

Background Art

[0002] For Eu^{2+} -doped material normally UV-blue emission is observed (Blasse and Grabmeier: Luminescent Materials, Springer Verlag, Heidelberg, 1994; in the following cited under D1). Several studies show that also emission in the green and yellow part of the visible spectrum is possible (Blasse: Special Cases of divalent lanthanide emission, Eur. J. Solid State Inorg. Chem. 33 (1996), p. 175; Poort, Blokpoel and Blasse: Luminescence of Eu^{2+} in Barium and Strontium Aluminate and Gallate, Chem. Mater. 7 (1995), p. 1547; Poort, Reijnhoudt, van der Kuip, and Blasse: Luminescence of Eu^{2+} in Silicate host lattices with Alkaline earth ions in a row, J. Alloys and Comp. 241 (1996), p. 75). Hitherto, red Eu^{2+} luminescence is observed only in some exceptional cases, such as in alkaline earth sulphides and related lattices of the rock-salt type (Nakao, Luminescence centers of MgS, CaS and CaSe Phosphors Activated with Eu^{2+} Ion, J. Phys. Soc. Jpn. 48(1980), p. 534), in alkaline earth thiogallates (Davolos, Garcia, Fouassier, and Hagenmuller, Luminescence of Eu^{2+} in Strontium and Barium Thiogallates, J. Solid. State Chem. 83 (1989), p. 316) and in some borates (Diaz and Keszler; Red, Green, and Blue Eu^{2+} luminescence in solid state Borates: a structure-property relationship, Mater. Res. Bull. 31 (1996), p. 147). Eu^{2+} luminescence in alkaline-earth silicon nitrides has hitherto only been reported for $MgSiN_2$:Eu (Gaido, Dubrovskii, and Zykov: Photoluminescence of $MgSiN_2$ Activated by Europium, Izv. Akad. Nauk SSSR, Neorg. Mater. 10 (1974), p. 564; Dubrovskii, Zykov and Chernovets: Luminescence of rare earth Activated $MgSiN_2$, Izv. Akad. Nauk SSSR, Neorg. Mater. 17 (1981), p. 1421) and $Mg_{1-x}Zn_xSiN_2$:Eu (Lim, Lee, Chang: Photoluminescence Characterization of $Mg_{1-x}Zn_xSiN_2$:Tb for Thin Film Electroluminescent Devices Application, Inorganic and Organic Electroluminescence, Berlin, Wissenschaft und Technik Verlag, (1996), p. 363). For both Eu^{2+} luminescence in the green and green/blue part of the spectrum was found.

[0003] New host lattices of the nitridosilicate type are based on a three dimensional network of cross-linked SiN4 tetrahedra in which alkaline earth ions (M= Ca, Sr and Ba) are incorporated. Such lattices are for example $Ca_2Si_5N_8$ (Schlieper and Schlick: Nitridosilicate I, Hochtemperatursynthese und Kristallstruktur von $Ca_2Si_5N_8$, Z. anorg. allg. Chem. 621, (1995), p. 1037), $Sr_2Si_5N_8$ and $Ba_2Si_5N_8$ (Schlieper, Millus and Schlick: Nitridosilicate II, Hochtemperatursynthesen und Kristallstrukturen von $Sr_2Si_5N_8$ and $Ba_2Si_5N_8$, Z. anorg. allg. Chem. 621, (1995), p. 1380), and $BaSi_7N_{10}$ (Huppertz and Schnick: Edge-Sharing SiN_4 tetrahedra in the highly condensed Nitridosilicate $BaSi_7N_{10}$, Chem. Eur. J. 3 (1997), p. 249). The lattice types are mentioned in Table 1.

[0004] However, sulfide based phosphors (e.g. earth alkaline sulfides) are less desirable for lighting applications, especially for LED applications, because they interact with the encapsulating resin system, and partially suffer from hydrolytic attack. Red emitting Eu^{2+} activated borates show already concentration quenching to a certain degree at the operating Temperature of LEDs.

Disclosure of the Invention

[0005] It is, therefore, an object of this invention to obviate the disadvantages of the prior art. It is another object of the invention to provide a red emitting luminescent material which is excitable at wavelengths around 300 to 500 nm, together with high chemical and thermal stability.

[0006] Especially high stability up to at least 100 °C is highly desirable for LED applications. Their typical operation Temperature is around 80 °C.

[0007] These objects are accomplished by the characterising features of claim 1. Advantageous embodiments can be found in the dependant claims.

[0008] The new Eu^{2+}-doped luminescent materials show special long wavelength red emission. These phosphors are based on alkaline-earth silicon nitride material as host-lattices. They are very promising for LED applications. Hitherto white LEDs were realised by combining a blue emitting diode with a yellow emitting phosphor. Such a combination has only a poor colour rendition. A far better performance can be achieved by using a red-green-blue system. However, up to now, no candidate for a red phosphor excitable by short wavelength radiation around 450 nm could be found. The new material is the first one. Typically it can be used together with a green-emitting phosphor, for example strontiumaluminate $SrAl_2O_4:Eu^{2+}$, whose emission maximum is around 520 nm.

[0009] In detail, the new Red Emitting Luminescent Material, uses a host lattice of the nitridosilicate type $M_xsi_yN_z$: Eu, wherein M is at least one of an alkaline earth metal chosen from the group Ca, Sr, Ba and wherein $z = 2/3x + 4/3y$.

The incorporation of nitrogen increases the proportion of covalent bond and ligand-field splitting. As a consequence this leads to a pronounced shift of excitation and emission bands to longer wavelengths in comparison to oxide lattices.

[0010] Preferably, the red emitting luminescent material is of the type, wherein $x = 2$, and $y = 5$.

[0011] In another preferred embodiment, the red emitting luminescent material is of the type, wherein $x = 1$, and $y = 7$.

[0012] Preferably, the metal M in the red emitting luminescent material is strontium because the resulting phosphor is emitting at relatively short wavelengths. Thus the efficiency is rather high in comparison to most of the other metals.

[0013] In a further embodiment the red emitting luminescent material uses a mixture of different metals, for example Ca (10 atom.-%) together with Ba (balance), as component M.

[0014] These luminescent materials show high absorption and good excitation in the UV and blue visible spectrum (up to more than 450 nm), high quantum efficiency and low temperature quenching up to 100 °C.

[0015] It can be used for luminescence conversion LEDs with a blue light emitting primary source together with one or more phosphors (red and possibly additionally green).

Brief Description of the Drawings

[0016]

Fig. 1: Diffuse reflection spectra of undoped $Ba_2Si_5N_8$ and $Ba_2Si_5N_8$:Eu;

Fig. 2: Diffuse reflection spectra of undoped $BaSi_7N_{10}$ and $BaSi_7N_{10}$:Eu;

Fig. 3: Emission spectrum of $Ba_2Si_5N_8$:Eu;

Fig. 4: Emission spectrum of $BaSi_7N_{10}$:Eu;

Fig. 5: Emission spectrum of $Sr_2Si_5N_8$:Eu.

Detailed Embodiments

[0017] Eu_2O_3 (with purity 99,99 %), or Eu metal (99,99 %), Ba metal (> 99 %); Sr metal (99 %), Ca_3N_2 (98 %), or Ca powder (99,5%) and Si_3N_4 (99,9 %) were used as commercially available starting materials. Ba and Sr were nitrided by firing at 550 and 800 °C under a nitrogen atmosphere. Subsequently, Ca_3N_2 or nitrided Ba, Ca or Sr were ground in a mortar and stoichiometrically mixed with Si_3N_4 under nitrogen atmosphere. The Eu-concentration was 10 atom.-% compared to the alkaline earth ion. The powdered mixture was fired in molybdenum crucibles at about 1300-1400 °C in a horizontal tube furnace under nitrogen/hydrogen atmosphere. After firing, the powders were characterised by powder X-ray diffraction (Cu, Kα-line), which showed that all compounds had formed.

[0018] The undoped $Ba_2Si_5N_8$, $Ca_2Si_5N_8$ and $BaSi_7N_{10}$ are greyish-white powders. As expected, the undoped rare-earth activated silicon oxynitrides show high reflection in the visible range (400-650 nm) and a strong drop in the reflection between 250-300 nm (Fig. 1 and 2). The absorption is ascribed to host-lattice excitation. The Eu-doped samples are orange-red, except for $BaSi_7N_{10}$:Eu which is orange-yellow (Table 1). The strong coloration is unique for Eu^{2+}-doped rare-earth activated silicon oxynitrides and make these material interesting orange-red pigments. A typical example of a reflection spectrum of $Ba_2Si_5N_8$:Eu shows that the absorption due to Eu is superposed on the host-lattice absorption and extends up to 500-550 nm (Fig. 1). This explains the red-orange colour of these compounds. Similar reflection spectra were observed for $Ba_2Si_5N_8$:Eu and $Ca_2Si_5N_8$:Eu.

[0019] For $BaSi_7N_{10}$:Eu the absorption of Eu is less far in the visible part (Fig. 2), which explains the orange-yellow colour of this compound.

[0020] All samples show efficient luminescence under UV excitation with emission maxima in the red part of the visible spectrum (see Table 1). Two typical examples of emission spectra can be seen in Figs. 3 and 4. They show that the emission is at extremely long wavelengths (for Eu^{2+} emission) with maxima up to 660 nm for $BaSi_7N_{10}$:Eu (Fig. 4.). Excitation bands are observed at low energy which is the result of a centre of gravity of the Eu^{2+} 5d band at low energy and a strong ligand-field splitting of the Eu^{2+} 5d band, as can be expected for N^{3-} containing lattices (van Krevel, Hintzen, Metselaar, and Meijerink: Long Wavelength Ce^{3+}-luminescence in Y-Si-O-N Materials, J. Alloys and Comp. 168 (1998) 272).

[0021] Since these materials can convert blue into red light due to low-energy excitation bands, they can be applied in white light sources, for example based on primarily blue-emitting LED's (typically GaN or InGaN) combined with red, yellow and/or green emitting phosphors.

Table 1:

Compound	Crystal structure	Colour	Emission Maximum (nm)
$Ba_2Si_5N_8$:Eu	Monoclinic	Orange-Red	620
$Sr_2Si_5N_8$:Eu	Orthorhombic	Orange-Red	625
$Ba_2Si_5N_8$:Eu	Orthorhombic	Orange-Red	640
$BaSi_7N_{10}$:Eu	Monoclinic	Orange-Yellow	660

[0022] These emission maxima are unusually far in the long wavelength side. A specific example is a phosphor of the type $Sr_{1.8}Eu_{0.2}Si_5N_8$. Its emission spectrum is shown in fig. 5.
[0023] Another embodiment for realising M is using Zn that can replace Ba, Sr or Ca fully or partially.
[0024] A further embodiment for replacing Si fully or partially is Ge. An concrete embodiment is $Sr_{1.8}Eu_{0.2}Ge_5N_8$.

Claims

1. Red Emitting Luminescent Material, characterised in a host lattice of the nitridosilicate type $M_xSi_yN_z$:Eu, wherein M is at least one of an alkaline earth metal chosen from the group Ca, Sr, Ba, Zn and wherein $z = 2/3x + 4/3y$.

2. Red emitting luminescent material according to claim 1, wherein $x = 2$, and $y = 5$.

3. Red emitting luminescent material according to claim 1, wherein $x = 1$, and $y = 7$.

4. Red emitting luminescent material according to claim 1, wherein M is strontium.

5. Red emitting luminescent material according to claim 1, wherein M is a mixture of different metals.

6. Red emitting luminescent material according to claim 1, wherein Si is replaced fully or partially by Ge.

7. Light source with a red emitting luminescent material according to one of the precedent claims.

8. Light source of claim 6 wherein the primary emitted light is blue and the red emitting luminescent material is combined with a green emitting phosphor in order to secondary emitting white light.

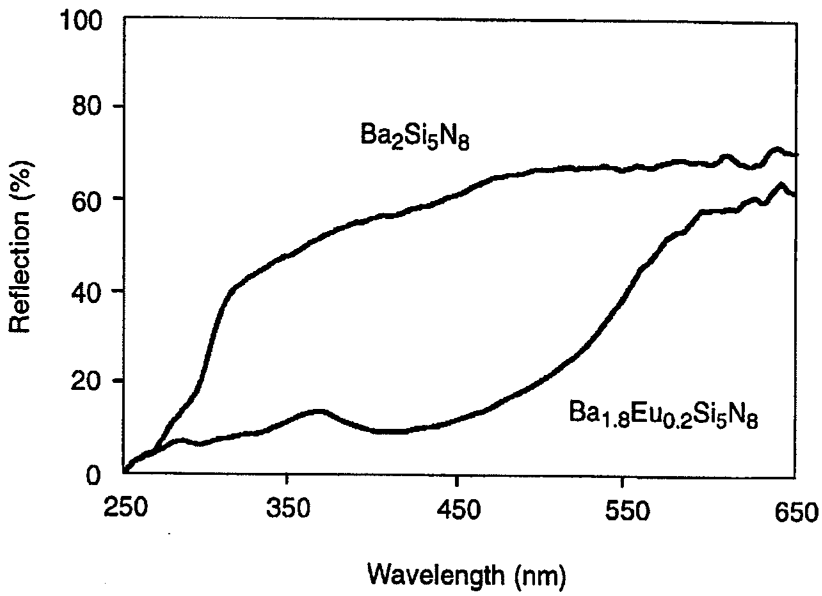
100
80
60
40
20
0
Reflection (%)
$Ba_2Si_5N_8$
$Ba_{1.8}Eu_{0.2}Si_5N_8$
250
350
450
550
650
Wavelength (nm)

FIG. 1

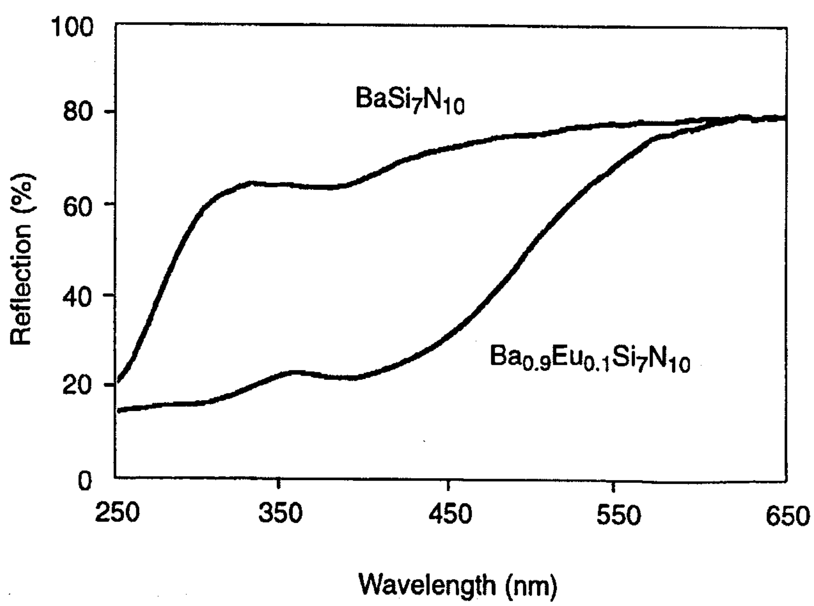
100
80
60
40
20
0
Reflection (%)
$BaSi_7N_{10}$
$Ba_{0.9}Eu_{0.1}Si_7N_{10}$
250
350
450
550
650
Wavelength (nm)

FIG. 2

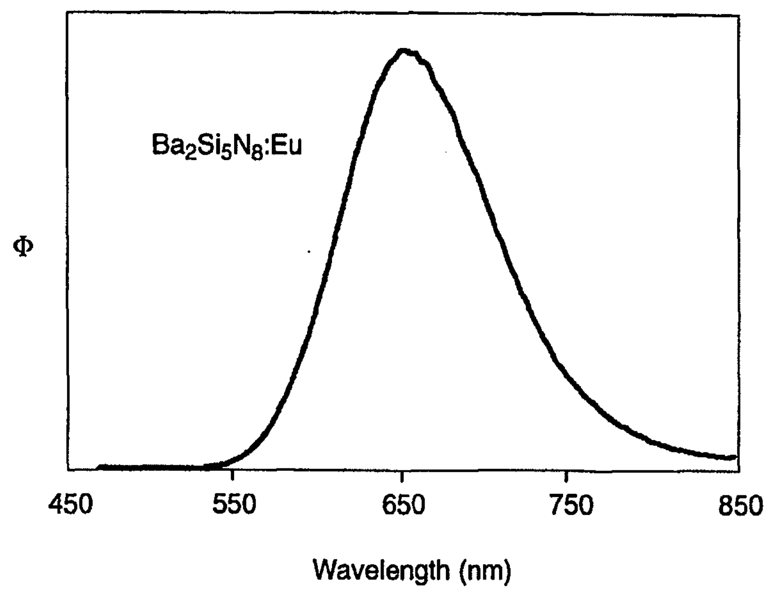
Ba2Si5N8:Eu
Φ
450
550
650
750
850
Wavelength (nm)

FIG. 3

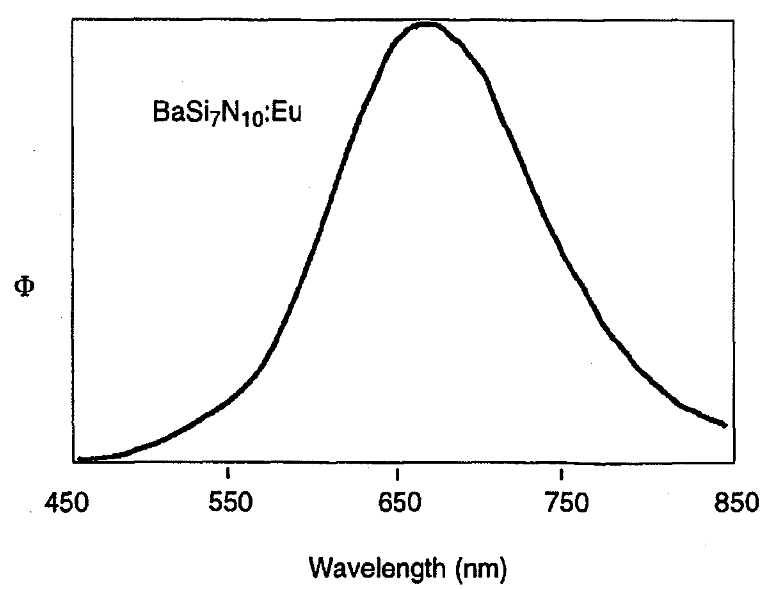
BaSi7N10:Eu
Φ
450
550
650
750
850
Wavelength (nm)

FIG. 4

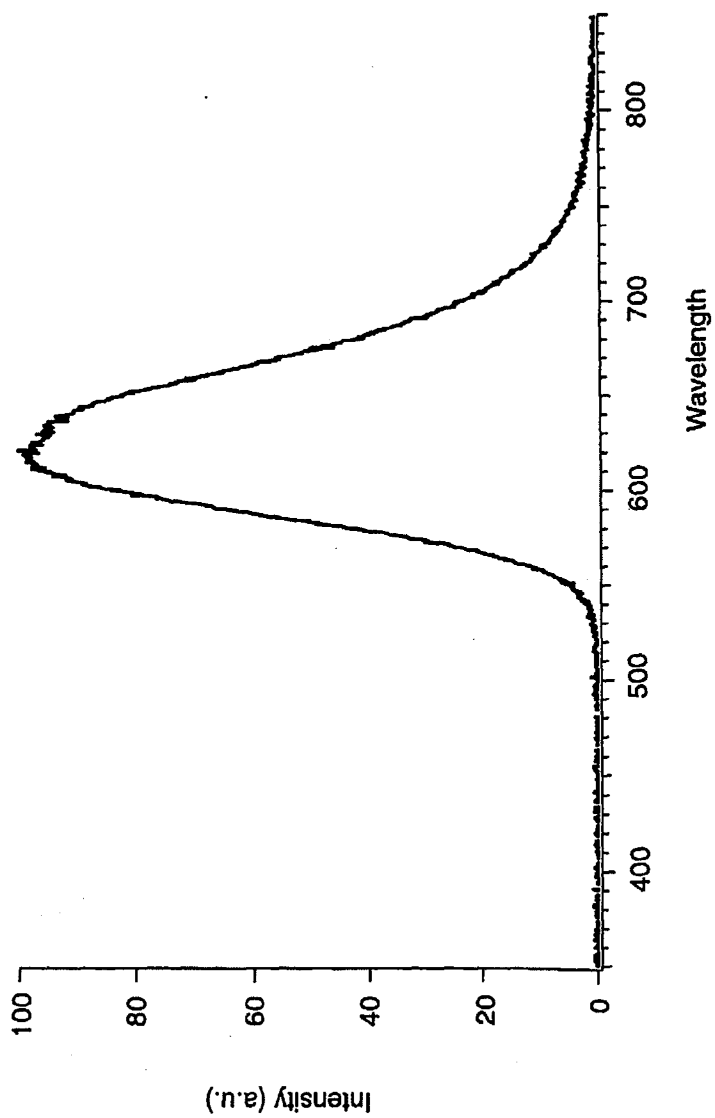

FIG. 5

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 99 12 3747

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
A	SOON-SEOK LEE ET AL: "Development and luminescent characteristics of CaSiN/sub 2/ based phosphors" JOURNAL OF THE INSTITUTE OF ELECTRONICS ENGINEERS OF KOREA D, OCT. 1999, INST. ELECTRON. ENG. KOREA, SOUTH KOREA, vol. 36-D, no. 10, pages 31-36, XP002136109 ISSN: 1226-5845	1-8	C09K11/79
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
			C09K

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	19 April 2000	Drouot, M-C

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P04C01)